Technical Report for Symposium G, "Fullerenes and Related Materials"

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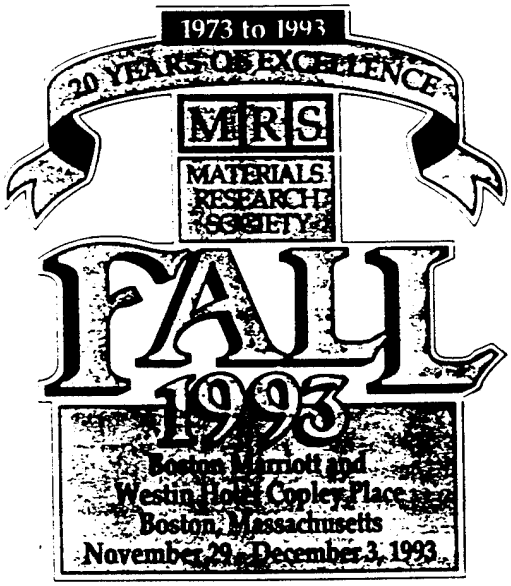


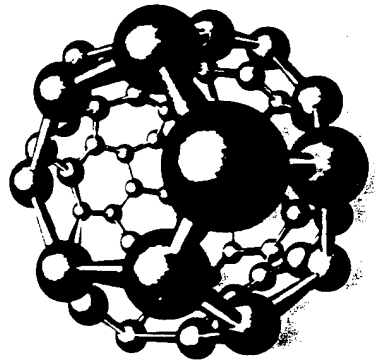

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# Symposium G: Fullerenes and Related Materials

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## G: FULLERENES AND RELATED MATERIALS

The Fullerenes and Related Materials Symposium consisted of 141 presentations comprised of 81 talks and 60 poster presentations. Fifteen of the talks were invited. In addition, two of the speakers, Donald Huffman and Wolfgang Kratschmer, received the MRS Medals after one of the Fullerene Symposia. This symposium enjoyed the presence of all of the original researchers who are credited with the discovery of "Buckyball" with the exception of Harry Kroto. The attendance for the opening session was approximately 500, falling to roughtly 300 for subsequent sessions.

The Fullerenes and Related Materials Symposium began with a brief history of the fullerene field and its role in the MRS Fall Meeting, where the very first results in this new field exploded onto the scene three years ago. The Fall 1993 meeting represented an opportunity to reflect on how the field has developed and where it may be headed. A number of speakers addressed the general question, "What are $C_{60}$ and other fullerenes good for?" Among those applications mentioned were lubricants, storage batteries, diamond films, hydrogen storage, ink additives, superconductors, and rocket propulsions.

One group reported that fullerenes "....work well as a lubricant in low humidity vacuums and may be a candidate for precision lubrication uses in space." The authors further report that the fullerene molecules loosely bond together to form "clusters" resembling blackberries. When the pressure and friction grew great enough to collapse these clusters, the remaining individual spherical molecules continued to provide the rolling, lubrication effect.

Reference was also made to the exciting applications of fullerenes as an antiviral agent. Emerging biomedical applications of fullerenes will likely be prominent in future MRS meetings..

Wolfgang Krätschmer and Donald R. Huffman, the first to produce macroscopic quantities of fullerenes and to demonstrate a new form of crystalline carbon, presented their MRS Medal acceptance speeches at this symposium and underlined the fruitful interaction of fullerene science and astrophysics. Although it appears unlikely that the presence of $C_{60}$ in space is responsible for the unidentified interstellar absorptions, the possibility was ventured that the higher fullerenes and "bucky onions" might account for some of these features. Bucky onions as large as 500 A° diameter (70 spherical shells) were reported. Further search of the discharge soot, "the mother of all fullerenes," was encouraged for other carbon-based molecules, especially small carbon-hydrogen radical clusters. It is ironical that although small fullerenes are apparently not responsible for the unidentified absorption features, the further development of the fullerene field has produced new carbonaceous material which may in fact account for the mysterious interstellar medium.

Continued characterization and improvement of the Krätschmer-Huffman fullerene generation technique was prescribed, especially methods for continuous generation of large amounts of fullerenes without interruption for reloading the graphite rods. Emphasis was placed on the passage of gas through the arc-discharge in order to quickly remove the fullerenes from the

destructive "hot" arc discharge and photon flux. Combustion synthesis of fullerenes in a premixed flame produced "soot" with 20 to 30% fullerene. The $C_{60}$ / $C_{70}$ ratio could be altered by varying the flame conditions and there were discussions of the mechanisms of fullerene formation and degradation. In the separations area, a method for the vapor phase gradient separation and purification of $C_{60}$ was presented. In addition, a metalloporphyrin-based stationary phase preparative column was shown to be particularly well-suited for fullerene separations. A method for the chromotographic separation of "giant" fullerenes was also discussed.

A number of groups reported on structural and physical properties of the so-called carbon nanotubes, including the single-walled nanotubes grown in carbon arcs containing $C_{60}$ and Fe or Co atoms. Theoretical considerations predict that the electrical conductivity of the nanotubes depends on the chiral "pitch" of the helical nanotubes (achiral tubes are metals and helical structures are semi-conductors). Single crystals of copper were reported to be encapsulated in buckytube derivatives.

The first Raman spectrum of nanotubes was of particular interest. The four intense Raman lines were remarkably insensitive to the diameter of the buckytubes. The most intense feature was split into two lines (1591 $cm^{-1}$ and 1569 $cm^{-1}$ ) as a result of the right-left helicity of the chiral nanotubes.

A number of potential applications of nanotubes were suggested, including hydrogen storage, nanowires, catalysis, seeds for the growth of fibers, and as a template for the growth of nerve fibers.

Laser ionization of fullerenes is well-known to exhibit an unusual "delayed" ionization in which electrons are emitted from the graphite spheres long after (microseconds) pulsed laser excitation, although this unusual behavior is generally ascribed to thermionic emission (i.e., the laser heats the graphite ball to a temperature sufficient to boil off electrons). An alternative interpretation of the delayed emission was described which involves the simultaneous excitation of as many as four Frenkel excitons on one $C_{60}$ molecule. Delayed ionization thus results from multiple exciton annihilation.

Several papers dealt with the electronic and vibronic properties of the fullerenes and fullerides. The structural properties of the various fullerenes of $C_{60}$ and $C_{70}$ were presented and the effects of pressure and dopant on the ordering transitions were discussed. Many papers dealt with the interaction of fullerenes with surfaces and their properties as multilayers and as superlattices. The mechanism of superconductivity was examined, and the first rare earth (Yb) doped fullerene superconductor was reported (Tc = 5.7°K). A new synthesis route using thermal decomposition of azides was shown to give samples with high shielding characteristics. A theoretical description of a $C_{60}$ - graphite intercalation compound doped with potassium exhibited a high density of states at the Fermi level and offers promise as a high-Tc superconductor.

The fullerene-related materials, such as bucky-onions, spheroids (spherical particles), nanotubes, and endohedral metallofullerenes, have gained special interest in the present symposium. These materials are considered as "fullerene-related" ones, but the formation, structures, and

electronic/solid state properties are completely different from the so-called fullerenes, providing special interests to researchers in many fields of material sciences.

Daniel Ugarte talked about bucky-onions (graphitic onion-like particles) which are generated as a result of the coalescence of nano-meter scale carbon particles under electron beam irradiation. High energy electron bombardment generates, as an exclusive product, graphitic onion-like particles (concentric arrangement of fullerenes) with a remarkable spherical shape. Ugarte showed us a video which visualized in its real time the transformation of the carbon particles to buckyonions. As discussed above, Ugarte and Krätschmer emphasized that certain buckyonions represent important candidates for the origin of the unidentified interstellar absorption at 220 nm.

One of the other important developments in the field of fullerene science discussed in the present symposium was the successful characterization of endohedral metallofullerenes. Endohedral metallofullerenes have gained wide interest as a result of their unique electronic and structural properties. In this regard, a number of researchers reported the isolation and characterization of scandium ($Sc_2$ @ $C_{82}$ , $Sc_3$ @ $C_{82}$ ) and lanthanum (La @ $C_{82}$ ) fullerenes. Scanning tunneling microscopy (STM) of $Sc_2$ @ $C_{82}$ deposited on the Si (100) 2x1 clean surface indicated an approximately spherical structure of $Sc_2$ @ $C_{82}$ and of a small band gap as compared with those of other fullerenes, indicating the possibility of high electrical conductivity. The STM and TEM results showed that the metal atoms are indeed trapped within the carbon cage, confirming previous studies.

In summary, the Fall 1993 meeting contained a healthy mix of past and present fullerene research developments. Special attention was given to potential applications of fullerenes. The meeting reflected the continued optimism of this area of science which continues to bring together a very broad admixture of chemists, physicists, and biologists to bear upon problems in material science.